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INITIATION OF DEFLAGRATION WAVES AT SURFACES OF

AMMONIUM PERCHLORATE-COPPER CHROMITE-CARBON PELLETS

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ABSTRACT

A study was made of the initiation of a deflagration wave
at the surface of ammonium perchlorate-copper chromite-carbon
pellets in nitrogen at 25 atmospheres. The relationship
between energy flux density I and exposure time τ_I, which
defines the family of boundary conditions necessary and suf-
ficient to cause initiation, was measured. Theoretical analy-
sis was made by means of the partial differential equation which
describes the space-time temperature distribution in the pellet
in terms of chemical reaction rate, heat of reaction, thermal
conductivity, heat capacity, optical absorptivity, and surface
reflectivity. Integration of the equation using the experi-
mentally determined chemical and physical parameters and bound-
ary conditions gave the temperature of the pellet -- and in
particular the temperature of the pellet surface -- as a function
of time, with flux as a parameter. From this solution one

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obtained for given flux density (a) the temperature $T(0,\tau_I)$ of the initiating surface at the moment τ_I of cut-off of the energy pulse, and (b) a lower bound for the minimum thermal ignition time τ_{im}.

$T(0,\tau_I)$ for ammonium perchlorate with 5% copper chromite was 380 ± 31°C. It was drastically lowered when carbon was added, the amount of lowering being proportional to carbon concentration. It ranged from 300 to 215°C for carbon percentages ranging from 0.5 to 4. For given composition $T(0,\tau_I)$ was independent of flux density over the range 9 to 63 cal/cm²-sec. Initiation occurred substantially before the calculated minimum thermal ignition time τ_{im}. The results provide support for the view that thermal ignition of the solid material is not a prerequisite for initiation of a deflagration wave.

I. INTRODUCTION

The word ignition, applied to condensed materials, is commonly used in two contexts: thermal ignition, and initiation of a deflagration wave at a surface. Thermal ignition describes the end result of the sequence of events: Heat introduced from an external source plus heat generated by exothermic reactions of the solid, is greater than heat loss; with a positive and usually exponential dependence of rate on temperature, the reaction rate and the temperature rise continually increase; because of the exponential dependence, the fraction reacted increases slowly for a length of time dependent on the temperature, then rapidly approaches unity

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over a narrow time interval; the going-to-completion is thermal ignition, and the time between the initial heat input and ignition is the induction time. Ignition in the second sense means the end result of a sequence which includes at least (a) the formation of gases from the solid, (b) their exothermic reaction, and (c) the establishment at the surface of a steady gaseous deflagration wave which continues to propagate as a wave throughout the entire mass after removal of the external source of energy.

According to one theory thermal ignition in a solid layer near the surface is a prerequisite for initiation of a deflagration wave. Frazer and Hicks[1] and Hicks[2] described a theoretical model for initiation based on this postulate. The model was stated in terms of the time-dependent differential equation governing temperature in a one-dimensional semi-infinite slab which was heated (a) uniformly over the surface by conduction, and (b) internally by an exothermic chemical reaction whose rate depended exponentially on temperature. They provided a detailed analysis of the time-space temperature behavior of this system. Altman and Grant[3] measured the ignition times of ammonium perchlorate-fuel binder slabs which were ignited by a hot wire whose rate of heat production was known. Temperature at ignition was computed from these data and the same partial differential equation, but without the chemical reaction term. They postulated that a solid exothermic reaction occurred at a rapid rate in a

1. J. H. Frazer and B. L. Hicks, J. Phys. and Coll. Chem. 54, 872 (1950)

2. Bruce L. Hicks, J. Chem. Phys. 22, 414 (1954)

3. D. Altman and A. F. Grant, Jr., Fourth Symposium (International) on Combustion, The Williams and Wilkins Company, Baltimore, 1953, p. 158

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narrow temperature interval which could be approximated by a step function, so that the lower bound of the discontinuity was the ignition temperature-ignition time point. Theory and experiment correlated when an ignition temperature of about 390°C at all power inputs was assumed.

An alternative view is that thermal ignition of the solid is not necessarily required for initiation, but that in at least some cases the sequence may be the formation from the solid, in a reaction possibly endothermic, of reactive gases followed by their thermal ignition to form the deflagration wave. Jones[4] investigated the physical factors -- geometrical, thermal, and electrical -- affecting the initiation of deflagration in several explosive materials by heated filaments imbedded in the medium. He concluded that under his conditions the temperature of the solid was the critical factor rather than the attainment of a high rate of exothermic solid phase reaction, and that the criteria for initiation were fulfilled before such a reaction began. Rideal and Robertson[5] suggested that initiation of a deflagration wave at a nitrocellulose surface occurred by a two-step sequence consisting of formation of reactive gases by thermal decomposition of the condensed phase followed by ignition of the gases. McAlevy and Summerfield[6] in studying initiation by a gas shock wave of double base propellant in an atmosphere of O_2-N_2 mixtures reached a similar conclusion.

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4.   E. Jones, Proc. Roy. Soc. (London) 198A, 523 (1949)

5.   E. K. Rideal and A. J. B. Robertson, Third Symposium on Combustion and Flame and Explosion Phenomena, The Williams and Wilkins Company, Baltimore, 1949, p. 536

6.   R. F. McAlevy, III and M. Summerfield, ARS Journal 32, 270 (1962)

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We have attempted to investigate this question for one chemical system by studying surface initiation by a single pulse of known energy flux density and duration introduced into a pellet of material for which physical parameters and reaction heats and rates have been measured. From a solution of the governing partial differential equation including an appropriate chemical reaction term, and the experimental value of the pulse duration required for initiation with given flux density, one obtains the temperature of the initiating solid surface at the moment of cut-off of the energy pulse. In addition, the relationship of this temperature-time point with reference to the point of minimum thermal ignition time is found.

Our study differs from the previous studies in one or more of the following ways. A deflagration wave is clearly formed at a surface as the end result of the process studied. Initiation occurs in a neutral gas atmosphere, so that complicating heat generation involving reaction of chemicals not generated by the solid is avoided. Initiation and deflagration occur at the constant pressure maintained in the apparatus, so that no energy is used in raising ambient pressure (by formation of gases) above a minimum pressure limit for steady deflagration. The system is closely approximated by the one-dimensional semi-infinite slab described by the equation. The magnitude and duration of the energy flux density pulse and the values of the physical parameters are measured. The flux density is varied over a seven-fold range. Heat release and rate of the exothermic reaction, which are used in the solution of the equation, are based on published data. The equation is solved numerically, so that only minor approximations, whose effects can be shown to be small, are needed.

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II. EXPERIMENTAL PROCEDURE

The chemical system was a mixture of ammonium perchlorate, copper chromite, and carbon. Copper chromite, a propellant burning-rate catalyst, analyzes as 82% CuO, 17% Cr_2O_3, and 1% impurities. Pelleted ammonium perchlorate containing carbon and copper chromite totaling 3 to 7% will deflagrate at 25 atmospheres in nitrogen. We found that following ignition at this pressure ammonium perchlorate would not consistently support a steady deflagration in the absence of copper chromite; carbon was not essential for steady deflagration. (Levy and Friedman[7] reported steady deflagration of ammonium perchlorate, without additives, in nitrogen at 22 atmospheres. On the other hand Adams, Newman, and Robins[8] reported a lower pressure limit of deflagration of 68 atmospheres, and Arden, Powling, and Smith[9] found 102 atmospheres. The differences in observed pressure limit may be due to differences in particle size distribution, small amounts of catalysts, or convective and radiative heat losses.)

The copper chromite was Harshaw Chemical Company Cu-0202-p, material, with a 50% point (by weight) grain size of 3.7μ. The carbon was Cabot Incorporated furnace black Sterling VR, with a mean ultimate particle

7. J. B. Levy and Raymond Friedman, Eighth Symposium (International) on Combustion, The Williams and Wilkins Co., Baltimore, 1962, p. 663

8. G. K. Adams, B. H. Newman, and A. B. Robins, Eighth Symposium (International) on Combustion, ibid., p. 693

9. E. A. Arden, J. Powling, and W. A. W. Smith, Combustion and Flame 6, 21 (1962)

diameter of 51 millimicrons and a surface area of 25 M^2/gm as determined
by nitrogen adsorption. The ammonium perchlorate was of reagent grade
(Matheson-Coleman-Bell), and was not recrystallized before use. It was
dried in a vacuum for 16 hours at 50°C prior to being ground in a micro-
pulverizer and screened to give the following weight size distribution:
50% through 150 mesh screen, on 200; 25% through 200 mesh, on 325; 25%
through 325 mesh. The materials were blended and again dried 16 hours
at 50°C. Cylindrical pellets 3.2 mm thick and 7.6 mm in diameter were
pressed at 93°C and 42,000 psi and stored in a desiccator until use.

The apparatus for providing the energy flux was a double-ellipsoidal
carbon arc image furnace,[10,11] shown schematically in Fig. 1. The radia-
tion wave length lies between 0.2 and 2.0 microns, peaking sharply between
0.4 and 0.6 micron. It is assumed that all absorbed energy is converted
into heat and that there is no important photochemical reaction. The
magnitude of flux density was adjusted by means of shutters (not shown
in Fig. 1) placed across one of the mirrors. The exposure time was con-
trolled by adjusting the speeds of rotation of three coaxial slotted disks
placed at the common focus between the mirrors. The beam converged in a
cone of 120 degree vertex angle to a roughly ellipsoidal image with axes
of approximately 1 cm. The pellet, inside a 1.26-cm internal diameter
Pyrex cylinder, was positioned so that a plane circular end received the

10. M. R. Null and W. W. Lozier, Rev. Sci. Instr. 29, 163 (1958)

11. N. K. Hiester and R. E. De La Rue, ARS Journ. 30, 928 (1960)

flux, with maximum flux density at the center. Through the cylinder

nitrogen flowed at 25 atmospheres pressure and a rate of 50-100 cc/min.

Edge effects were avoided by shielding the pellet edges from the beam.

The pellet surface was viewed by a photocell, which recorded the reflected

light from the received flux and from flame-associated reactions, making

possible a determination of the moment of initiation to within one milli-

second. Direction of propagation of the deflagration wave was horizontal.

The flux-calibrating calorimeter, described in detail elsewhere, [12]

was designed to fit inside the cylinder so that flux was measured after

it traversed the Pyrex wall. It consisted of a spherical segment of cop-

per which was blackened inside and had a thermocouple attached outside.

A silver foil shield with an aperture could be placed in front of the

blackened surface to limit and define a cross-section of the intercepted

beam. The radiation which passed through the aperture struck the black-

ened surface, causing a temperature rise of the segment, which was measured

by the thermocouple. Differentiation of the temperature-time curve gave

the pulse shape. Flux density was computed from temperature rise, time

of exposure, mass, heat capacity, and area of aperture. The spatial flux

distribution within the focal volume was mapped[12] with the calorimeter

and it was approximately symmetrical about the pellet center, falling off

to about 98% of maximum at a diameter of 1.25 mm, 96% at 2.5 mm, and 75%

at 5 mm. Over a circle of 2.5-mm diameter the flux density was constant

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12. R. B. Beyer, Leonard McCulley, and Marjorie W. Evans, "Measurement

    of Energy Flux Distribution in the Focus of an Arc Image Furnace,"

    Applied Optics, to be published.

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more than 95% of the exposure time, so that to a good approximation the pulse was square and the flux constant during exposure. Accuracy, taking into account both measurement error and variation of beam intensity over short intervals of time due to furnace fluctuation, was ± 5%.

III. EXPERIMENTAL RESULTS

Material Properties

Pellet densities, thermal conductivities, reflectances, transmittances, and heat capacities were measured. Densities were 1.97 ± 0.04 gm/cm^3. Thermal conductivities were 1.12 ± 0.03 x 10^{-3} cal/cm-sec-^{0}C. Spectral reflectances were measured at room temperature from 0.25 to 2.5 microns on a Beckman DK-2 Spectroreflectometer.[13] The total reflectance r, averaged over wave length, was 0.050 ± 0.005. Spectral transmittance was studied over the wave length range 0.34-1.0 micron on a Cary model 14 Recording Spectrophotometer, using sample thicknesses of 0.79 and 1.58 mm. Absorption coefficients for pure ammonium perchlorate pellets ranged from 5 x 10^3 cm^{-1} at a wave length of 1 micron to 1 x 10^5 cm^{-1} at 0.34 micron. When copper chromite or carbon was present the transmittance was so small that it could not be measured.

The heat capacity of each constituent was determined by measuring heat content in the range 25-350^{0}C using a drop calorimeter.[14] Calculation was on the basis of final weight of sample after heating to temperature

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13. Reflectance measurements were made by Mr. R. E. Rolling, Institute of Engineering Research, College of Engineering, University of California, Berkeley, California.

14. O. Kubaschewski and E. L. Evans, Metallurgical Thermochemistry, 3rd Ed., Pergamon Press, New York, 1958, pp. 102-4.

for 25-90 minutes in a furnace. Data are given in Fig. 2, with weight
loss during furnace heating given in parentheses. Copper chromite showed
no weight loss during the heating, and carbon < 1.5% at all temperatures.
Ammonium perchlorate showed a substantial weight loss above 240°C, and
a very large -- 2.7 kcal/mole -- heat of transition from orthorhombic to
cubic crystal structure at 240°C. The weight loss and the large transi-
tion heat might have been due to an exothermic decomposition during the
furnace heating, a decomposition which is known to occur to the extent
of 20-30% of the total material.[15] If, because of the reaction, the
remaining material were at a higher temperature than the furnace, the
apparent heat content would be too high at temperatures at which weight
loss occurred. Therefore, the experiments were repeated with salt which
had been preheated to remove the reactive material. They were also
repeated with twice-recrystallized salt, which exhibits a somewhat slower
decomposition rate[16] than unrecrystallized material.[17] The results were
the same in all three sets of experiments. The weight loss is thus pre-
dominantly due to sublimation. The value compares well with the value
2.3 ± 0.2 kcal/mole recently reported by Markowitz.[18]

15. L. L. Bircumshaw and B. H. Newman, Proc. Roy. Soc. (London) A227,
    115 (1954); A227, 228 (1955)

16. A. K. Galwey and P. W. M. Jacobs, Proc. Roy. Soc. (London), A254,
    455 (1960)

17. P. W. M. Jacobs and A. R. Tariq Kureishy, Eighth Symposium (Inter-
    national) on Combustion, The Williams and Wilkins Co., Baltimore,
    1962, pp. 672-677

18. JANAF Interim Thermochemical Tables, The Dow Chemical Company,
    Midland, Michigan

Initiation Measurements

At a given flux density entering the pellet surface, $I(1-4)$ cal/cm^2-sec, the minimum exposure time for initiation τ_I was determined. I is the maximum flux density intercepted, as determined by the calorimeter, and $(1-r)$ is the reflection correction factor. τ_I versus $I(1-r)$ data are given in Table I in columns 3 and 4. The notation AP/CC/C indicates the weight percent ratio of ammonium perchlorate/copper chromite/carbon. The uncertainties give the $\Delta\tau_I$ over which mixed results, both initiation and failure to initiate, were obtained.

Photoelectric observation showed that for exposure times greater than τ_I initiation occurred during exposure to flux, and for exposure time equal to τ_I initiation occurred with a delay of less than approximately one millisecond.

IV. ANALYSIS

The Governing Partial Differential Equation

If (a) transmittance is negligible, (b) the system is a one-dimensional semi-infinite slab, (c) the material is homogeneous, and (d) surface regression is negligible, then the differential equation describing the temperature history in the pellet is

$$c(T)\rho \, \frac{\partial T}{\partial t} \;=\; \lambda \, \frac{\partial^2 T}{\partial x^2} \;+\; Q(T) \, K(T,\epsilon) \tag{1}$$

with the initial and boundary conditions

$$-\lambda \, \frac{\partial T}{\partial x} \;=\; I(1-r) \qquad \text{at} \qquad x = 0$$

$$T = T_o \qquad \text{at} \qquad x = \infty$$

$$T = T_o \qquad \text{at} \qquad t = 0$$

The surface of the pellet is at x = 0, and the pellet extends in the direction of positive x . T is temperature, t time, λ thermal conductivity, ρ density, c heat capacity, Q heat of reaction with Q positive if the reaction is exothermic, I(1-r) the density of flux entering the surface, and K the rate of reaction which is equivalent to $d\epsilon/dt$, where ϵ is the fraction reacted.

If transmittance is not negligible the differential equation is

$$c(T)\rho \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + \alpha I(1-r)e^{-\alpha x} + Q(T) K(T,\epsilon) \qquad (2)$$

with the initial and boundary conditions

$$\frac{\partial T}{\partial x} = 0 \qquad\qquad \text{at} \quad x = 0$$

$$T = T_o \qquad\qquad \text{at} \quad x = \infty$$

$$T = T_o \qquad\qquad \text{at} \quad t = 0$$

Here α is the absorption coefficient. Equations (1) and (2) were solved numerically for typical cases, using in Eq. (2) the lowest value of α observed for pure ammonium perchlorate pellets, α = 5000 cm^{-1}. The solutions were identical at a flux density of 20 cal/cm^2-sec. At 100 cal/cm^2-sec, a higher flux density than any used in our experiments, a difference in temperature of less than 10 degrees was found at any given value of x. Since both the average value of the absorption coefficient of ammonium perchlorate and the coefficient for pellets containing copper chromite or carbon were substantially higher than 5000 cm^{-1}, it was concluded that transmittance could be neglected.

The semi-infinite approximation is valid if the rear surface of the pellet remains at the uniform initial temperature T_o throughout the

experiment. This can be tested by solving the equation which describes

the temperature history in a nonreacting one-dimensional semi-infinite

slab exposed to a constant energy flux density $I(1-r)$ [19]

$$T(x,t) - T_o = \frac{2\ I(1-r)\ \sqrt{\kappa t}}{\lambda}\ i\ \text{erfc}\ \frac{x}{2\sqrt{\kappa t}} \qquad (3)$$

where $\kappa = \lambda/\rho c$ is the thermal diffusivity. This equation was solved

for two extreme conditions using values of κ and λ appropriate for

the pellets; $\kappa = 1.42 \times 10^{-3}$ cm^2-sec and $\lambda = 1.12 \times 10^{-3}$ cal/cm-sec-$^\circ$C.

The conditions were $I(1-r) = 63$ cal/cm^2-sec, $t = 21$ msec; and $I(1-r) =$

18 cal/cm^2-sec, $t = 250$ msec. $(T-T_o)$ was found to be less than 0.8°C

at a position 0.22 mm from the surface in the first case and 0.76 mm from

the surface in the second case. Since the pellets used in the experiments

were 3.2 mm thick, the boundary condition $T = 0$ at $x = \infty$ is valid, and

the semi-infinite approximation is good.

The one-dimensional approximation is valid if lateral heat flow is

negligible. This can be tested by finding the temperature-time history

over the surface of a semi-infinite solid receiving a circle of constant

flux. Thomas[20] solved the problem in terms of $\kappa \tau / R_f^2$, where τ is

time of exposure, and R_f is the radius of the flux circle. His equa-

tions give the difference between the temperature of the center of the

heated area and the temperature which would have resulted if the heated

19. H. S. Carslaw and J. C. Jaeger, Conduction of Heat in Solids,
    Oxford University Press, 1948, p. 56, eq. 6

20. P. H. Thomas, Quart. Journ. of Mech. and App. Math. 9-10, 482 (1956-57)

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area had extended over the whole surface, i.e. had been a plane source producing one-dimensional flow. For $R_f = 0.064$ cm, the difference in temperature is found to be 5% for $\tau = 490$ msec, 1% for $\tau = 285$ msec, 0.2% for $\tau = 175$ msec, and correspondingly less for shorter exposure times. Most of our exposure times were less than 250 msec, so that the heat flow was linear and the one-dimensional approximation is justified.

The homogeneity approximation can be examined as follows: 93 to 97% of the material was ammonium particles of 75μ average diameter, these being coated with particles of 3.7μ copper chromite and 0.05μ carbon. Calculations show that about 0.5% carbon sufficed to cover with a one-particle layer all ammonium perchlorate surfaces, while the copper chromite was insufficient for complete coverage. Except for the case in which no carbon was present, the pellet surface thus consisted of a continuous layer of carbon under which lay ammonium perchlorate partially covered with 3.7μ copper chromite. The temperature of interest is that of the interface between the ammonium perchlorate and the additives, and in particular that of the interface nearest the pellet surface. Thus the solution of Eq. (1) for temperature at $x = 0$ is a good approximation if the temperature drop is negligible from $x = 0$ to the farthest distance within the pellet where a first ammonium perchlorate surface may be found, i.e. at $x = 3.7\mu$. For that part of the pellet surface where only carbon covers the ammonium perchlorate, the temperature drop is approximately 1/60 of this value. Appropriate solutions of Eq. (3) for a flux density of 18 cal/cm^2-sec showed a drop from $x = 0$ to 3.7μ of 6° at any time, with the drop proportional to $I(1-r)$. Thus for a flux of 100 cal/cm^2-sec

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the temperature drop was 30° at $x = 3.7\mu$, but only 0.2^o at $x = 0.05\mu$. One concludes that the approximation is good either for moderate fluxes or for low copper chromite content.

One must also justify the validity of the homogeneity approximation if, as has been suggested,[16] the solid phase exothermic reaction occurs on the intermosaic boundary surfaces of the ammonium perchlorate rather than uniformly throughout the particle. By the approximation it is assumed that the heat is rapidly distributed throughout the mosaic block so that temperature rises uniformly throughout the ammonium perchlorate particle, i.e., the temperature drop across 1.5μ is small. We saw that for the comparatively large flux density of 18 cal/cm^2-sec the temperature drop across 3.7μ was only 6°. Flux densities due to chemical reaction at intermosaic grain boundaries are readily estimated from molecular dimensions, heat of reaction, and the reaction rate values which are cited in later paragraphs. Over the temperature range of interest, shown later to be 20-400°C, they are found to be smaller than 18 cal/cm^2-sec by several orders of magnitude, so that the approximation is valid.

Gasification of ammonium perchlorate and consequent surface regression in the temperature range achieved by the pellet prior to initiation may occur by thermal decomposition and by sublimation. Computations based on the rate of the former, as set forth in subsequent paragraphs, and estimates based on the vapor pressure of the latter[21] indicate that during the time of an experiment, surface regression due to ammonium perchlorate gasification was less than 0.001μ.

21. S. H. Inami, W. A. Rosser, and Henry Wise, J. Phys. Chem. <u>67</u>, 1077 (1963)

In summary Eq. (1), for appropriate expressions of $Q(T)K(T,\epsilon)$, adequately describes the solid system during the period preceding initiation.

The Chemical Reaction

At temperatures of about 300°C and below, ammonium perchlorate decomposes by an exothermic reaction[15,16] which is conveniently referred to as the "low-temperature" reaction to distinguish it from another which occurs at higher temperatures. The products were found to be substantially accounted for by the equation

$$NH_4ClO_4(s) = \tfrac{1}{2} Cl_2 + \tfrac{3}{4} O_2 + 2 H_2O + \tfrac{1}{2} N_2O \qquad (4)$$
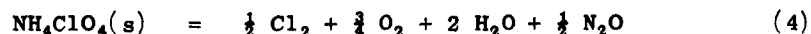
Reaction ceases after 20-30% of the material has decomposed, leaving the remaining perchlorate as a porous solid. This initial reaction involves the decomposition of intergranular material and it has been suggested that it occurs at intermosaic grain boundaries.[16] The rate of the low-temperature decomposition is little affected by commercial grade impurities,[17] Cr_2O_3,[22] CuO,[17,23] Cu_2O,[17,23] and copper chromite.[24] Twice-recrystallized ammonium perchlorate, with the data analyzed in terms of the Avrami-Erofeyev equation, gave a rate constant $k = 10^{9.6} e^{-30.1/RT}$ sec^{-1}, the units of the activation energy being kcal/mole. The highest rate cited was for ammonium perchlorate with commercial grade impurities which yielded $k = 10^{10.6} e^{-32.6/RT}$ sec^{-1}.

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22. A. Hermoni and A. Salmon, Eighth Symposium (International) on Combustion, The Williams and Wilkins Co., Baltimore, 1962, pp. 656-662

23. P. W. M. Jacobs and A. R. Tariq Kureishy, J. Chem. Soc. 1962, 556

24. P. W. M. Jacobs, private communication

If the temperature of the residue from this low-temperature reaction is raised to about 300°C or above, a further exothermic reaction becomes detectable which continues until decomposition is complete. This reaction apparently differs kinetically from the low-temperature reaction, and is conveniently referred to as the "high-temperature" reaction.[25] In fresh samples at 300°C or above both reactions can be followed kinetically.[24]

Carbon exhibits a different behavior. Galwey and Jacobs,[26] using sugar charcoal passing 85 mesh, found that below 240-260°C it had no detectable catalytic effect, but at higher temperatures an accelerated reaction was observed. Jacobs and Russell-Jones,[24] using a thermogravimetric technique, have recently measured the low-temperature and high-temperature decomposition rates at one atmosphere pressure in air of mixtures of unrecrystallized ammonium perchlorate, copper chromite, and carbon. The materials were the same used in our initiation studies, as described in the section on Experimental Procedure. Analyzing the low-temperature reaction data in terms of the Avrami-Erofeyev equation with n = 2, they found an activation energy lying between 31 and 32 kcal/mole and a frequency factor lying between $10^{9.8}$ and $10^{10.2}$ sec^{-1} under the following conditions: AP/CC/C = 100, 95/5/0, and 95/0/5 in the temperature interval 200-280°C; AP/CC/C = 95/2.5/2.5 in the temperature

25. A. K. Galwey and P. W. M. Jacobs, J. Chem. Soc. 1959, 837

26. A. K. Galwey and P. W. M. Jacobs, Trans. Far. Soc. 56, 581 (1960)

interval 200-235°C. The rate of decomposition by the high-temperature reaction was analyzed in terms of the contracting area equation. The results gave $k = 10^{7.1} e^{-31.6/RT}$ sec^{-1} for 100% ammonium perchlorate over the temperature range 280-380°C, and $k = 10^{14.0} e^{-47.0/RT}$ sec^{-1} for AP/CC/C = 95/5/0 and 95/0/5 over the range 235-320°C.

Thus at least up to 300°C the appropriate rate K in Eq. (1) is that for the low-temperature reaction. Even between 300°C and 400°C the rate for the low-temperature reaction is considerably faster, so that a solution using the low-temperature rate will be a good approximation in that temperature range also. Since during the ignition the total mass change is small, the kinetic expression can be approximated by a zero-order expression

$$K \equiv d\epsilon/dt = k = \nu \exp(-E_a/RT) \qquad (5)$$

The heat of reaction $Q(T)$ of the reaction of Eq. (4) can be represented, within 2%, by[27]

$$Q \text{ (cal/cc)} = 0.556\, T + 388 \qquad (6)$$

where T is expressed in degrees Kelvin.

The Numerical Solution

Equations (1), (5), and (6) combine to give the equation which was solved numerically:

$$c(T)\rho \frac{\partial T}{\partial x} = \lambda \frac{\partial^2 T}{\partial x^2} + (0.556\, T + 388)\nu \exp(-E_a/RT) \qquad (7)$$

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27. Data employed were taken from the JANAF Interim Thermochemical Tables, The Dow Chemical Company, Midland, Michigan.

with the initial and boundary conditions of Eq. (1). The parameter values employed were:

$$T_0 = 298°K$$

$$\rho = 1.97 \text{ g/cm}^3$$

$$\lambda = 1.12 \times 10^{-3} \text{ cal/cm-sec-}°C$$

$$c(T) = 298\text{-}513°K\text{---}0.309 \text{ cal/g/}°C$$

$$L (513°K)\text{---}21.8 \text{ cal/g} \quad \text{(heat of crystal structure transition)}$$

$$\text{above } 513°K\text{---}0.365 \text{ cal/g/}°C$$

$$I(1\text{-}r) = 9, 18, 36, 63, 100 \text{ cal/cm-sec}$$

$$E_a = \text{(a) } 31,500 \quad \text{(b) } 31,500 \quad \text{(c) } 26,500 \text{ cal/mole}$$

$$v = \text{(a) } 10^{10} \quad \text{(b) } 10^{12} \quad \text{(c) } 10^{10} \text{ sec}^{-1}$$

The first set of E_a and v are the experimentally determined values. The other sets were included to illustrate the effect on the solutions of altering v or E_a. The mathematical method of solving Eq. (7) with a heat capacity expression reflecting the discontinuous endothermic crystal structure change is outlined in the Appendix.

Figure 3 gives the results. It is a plot of the temperature at the surface, $T(0,t)$, as a function of time, with $I(1\text{-}r)$ as a parameter. Curves 1 are the solutions when the reaction term $Q(T)K(T)$ is omitted. Curves 2 which branch away from each curve 1 are the corresponding solutions for Eq. (7) with the values of v and E_a taken from the published rate data. The points of divergence occur where the reaction term makes an appreciable contribution to the temperature. Curves 3 give the results for $E_a = 31.5$ kcal/mole, $v = 10^{12}$ sec^{-1}; closely similar curves are obtained for $E_a = 26.5$ kcal/mole, $v = 10^{10}$ sec^{-1}.

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Hicks[2] has given a detailed discussion of the behavior to be expected of the temperature of a semi-infinite, exothermally-reacting solid, under the influence of external heating. In his terms, thermal ignition occurs when the surface attains a high rate of reaction and of temperature rise. Under the influence of external heating which is cut off at time τ_o, the temperature of the surface rises monotonically until τ_o, after which there is cooling at the surface; subsequently the temperature goes through a minimum and eventually rises again until the ignition is reached at time τ_i. An adiabatic ignition time τ_{ia} occurs when there is no heat transfer at the surface and the temperature of the solid is uniform. Surface heating decreases ignition time τ_i from τ_{ia}. As heating time τ_o is increased, τ_o and τ_i approach equality with one another and with τ_{im}, the minimum ignition time. If heating time τ_o is even slightly below the minimum ignition time τ_{im}, then the ignition time τ_i increases very greatly.

The values of τ_I given in Table I are the particular values of cut-off times (i.e., exposure times) τ_o for which initiation occurs in our system. The delay time between cut-off and initiation was experimentally found to be less than one millisecond. The thin dashed line on Fig. 3 connects those points on the solution curves of Eq. (7) at which the temperature is $50^{\circ}C$ higher than the corresponding solution without reaction time. If we, with Hicks, define the thermal ignition time τ_i as that time at which the temperature-time curve is nearly vertical, then a line connecting the τ_{im} for the various flux densities will lie above this line.

From the solution curves of Fig. 3 and the values of $I(1-r)$ and τ_I in Table I, one finds the temperature of the initiating surface at the moment of cut-off, $T(0, \tau_I)$. Results are shown for each flux density in column 5 of Table I. Estimated error in calculated $T(0, \tau_I)$ varies with flux density and exposure time. The estimated error in I and in exposure time is ± 5%. The uncertainty in T_o was ± 3°C. The values of ρ, λ, c, and r are assumed in the solution of Eq. (7) to be the same for all compositions; in actuality they may vary from the average as follows: ρ ± 2%, λ ± 3%, c ± 1%, and $(1-r)$ ± 5%. For these errors in measurement the estimated error in calculated $T(0, \tau_I)$ is ± 35° for the composition which does not contain carbon (95/5/0), and ± 25° for all others. Dispersion of experimental results for single compositions would be expected to be, and is, smaller than the estimated error, as the dispersions in values of ρ, λ, c, and r are smaller.

Interpretation

Within the precision of the experiment, for given composition the temperature of the initiating surface at cut-off, $T(0, \tau_I)$, is seen from column 5 of Table I to be independent of flux density. The average values, with observed dispersions, are given in column 6.

Ammonium perchlorate containing 5% copper chromite has a value of $T(0, \tau_I)$ of 380 ± 31°C for flux densities of 18 and 63 cal/cm²-sec. The $T(0, \tau_I)$ points are shown as squares on Fig. 3, the dotted line between them being drawn at the average temperature. The value 380°C corresponds

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to the temperature at which Dode'[28] found that the salt deflagrated (380-390).

When carbon is added to the system, the temperature of the initiating surface at cut-off is drastically reduced. $T(0, \tau_I)$ appears to be principally a function of the carbon/ammonium perchlorate ratio, the value being lower the greater the carbon concentration. The results may be grouped as follows: For a C/AP ratio of 0.005, $T(0, \tau_I) = 298 \pm 12^oC$. For a ratio lying between 0.015 and 0.027, $T(0, \tau_I) = 254 \pm 24^oC$. For a ratio lying between 0.037 and 0.042, $T(0, \tau_I) = 214 \pm 14^oC$. In every case, for given composition, $T(0, \tau_I)$ is independent of flux density. A typical example is composition AP/CC/C = 95/2.5/2.5, for which the initiation points are shown on Fig. 3 as circles, the connecting dotted line being the average value 259 ± 15^oC.

$T(0, \tau_I)$ is independent of copper chromite concentration at constant carbon concentration, the value being 256 ± 25^oC for 2.5% carbon.

Knowing the minimum cut-off time which leads to initiation τ_I, one asks for the relationship of this time to a possible thermal ignition time τ_i. Hicks showed that thermal ignition time is a minimum τ_{im} when $\tau_o = \tau_i$. We know from experiment that initiation occurred less than one millisecond after cut-off, i.e., at about $\tau_I + 1$ msec. It is evident from Fig. 3 that $\tau_I + 1 \ll \tau_{im}$ for every flux density, i.e., that initiation time is much less than the minimum possible thermal ignition time. Hence, assuming the correctness of the rate data, the temperature of the surface at initiation is very nearly the temperature of the surface at cut-off, and initiation occurs before thermal ignition takes place.

28. M. Dode, C. R. Acad. Sci., Paris, **200**, 63 (1934); Bull. Soc. chim. Fr. (5) **5**, 170 (1938)

Should new information on the chemical kinetics of thermal decomposition indicate a higher pre-exponential factor or a lower activation energy, the minimum thermal ignition time might be brought into the range of observed τ_I. However, a thermal ignition mechanism predicts a thermal ignition temperature which varies with flux density, while our data indicate a constant initiation surface temperature over the range 9 to 63 cal/cm²-sec. (It is noted, though, that the variation of τ_{im} with flux density appears to become less pronounced at higher reaction rates.)

The results would therefore seem to support the view that for this system thermal ignition of the solid phase is not a necessary prerequisite of initiation of deflagration. Assuming the correctness of the alternative view that the critical process in initiation is the formation of reactive gases and their ignition, the chemical processes by which these reactive gases are formed are not yet clear. Nor are the roles of carbon and copper chromite made entirely clear by these results. However the fact that the heat release of the solid phase reaction is apparently unimportant in the initiation process suggests that their roles are associated with the gas phase reaction. The amount of carbon influences the surface temperature of initiation. It is possible that the carbon is involved in lowering the temperature at which reactive gases, perhaps NH_3 and decomposition products of $HClO_4$, are produced. The role of copper chromite appears to be different. Without it steady waves exist only at high pressures, and -- within the concentration range 0.5 to 4.5% -- a variation of concentration has no effect on surface initiation temperature. Its role therefore may be to lower the pressure limit for steady deflagration by catalyzing the gas phase reactions associated with the flame.

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ACKNOWLEDGMENTS

APPENDIX

Assume a homogeneous semi-infinite slab of material such that the heat capacity is c_1 or c_2 depending on whether the temperature is greater or less than T_c . Let the function $f(t)$ define the position of the phase change boundary at any time t . The temperatures $T_1(x,t)$ in the region $x \leq f(t)$ and $T_2(x,t)$ in $x \geq f(t)$ satisfy the following equations:

$$c_1\rho \frac{\partial T_1}{\partial t} = \lambda \frac{\partial^2 T_1}{\partial x^2} + (AT_1 + B) \nu e^{-E_a/RT_1} \qquad (1A)$$

$$-\lambda \frac{\partial T_1}{\partial x} = I_0 \qquad\qquad \text{at} \qquad x = 0$$

$$T_1 = T_c \qquad\qquad \text{at} \qquad x = f(t)$$

$$c_2\rho \frac{\partial T_2}{\partial t} = \lambda \frac{\partial^2 T_2}{\partial x^2} + (AT_2 + B) \nu e^{-E_a/RT_2} \qquad (2A)$$

$$T_2 = T_c \qquad\qquad \text{at} \qquad x = f(t)$$

$$T_2 = T_0 \qquad\qquad \text{at} \qquad x = \infty$$

$$T_2 = T_0 \qquad\qquad \text{at} \qquad t = 0$$

Conservation of energy at the phase change boundary requires

$$\lambda \frac{\partial T_2}{\partial x} - \lambda \frac{\partial T_1}{\partial x} = L\rho \, f'(t) \qquad\qquad \text{when} \quad x = f(t) \qquad (3A)$$

A large finite slab is used to approximate the semi-infinite model above, and the boundary condition of equation (2A) at $x = \infty$ is appropriately modified. With this finite model, standard numerical techniques are available so long as the surface temperature $T_1(0,t)$ is less than T_c (see for example "Difference Methods for Initial Value Problems," Chapter VI, R. D. Richtmyer, Interscience Publishers, 1957).
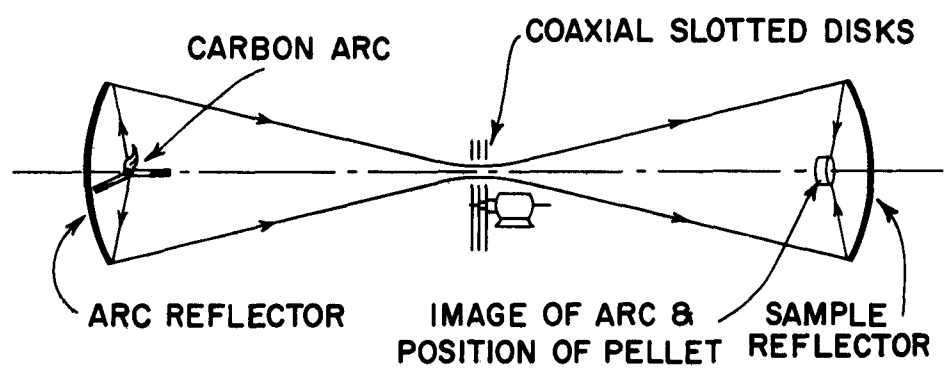
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The procedure when $T_1(0,t) \geq T_c$ is first to determine the position of the phase change boundary at the next point in time. This is accomplished for $T_1(0,t) = T_c$ with an analytic series representation of $f(t)$, and for $T_1(0,t) > T_c$ by an iteration scheme using the conservation of energy condition. Once the boundary position is known at this later time the problem separates into two subproblems. Each subproblem is restricted to one side of the phase change boundary and can be numerically integrated by the standard procedures indicated above.

Table I. Initiation Data and Calculated
Surface Temperature at Initiation

Set	Composition AP/CC/C	$I(1-r)$ cal/cm^2-sec	τ_I msec	$T(0,\tau_I)$ $^\circ$C	$\bar{T}(0,\tau_I)$ $^\circ$C
Constant CC + C	95/5/0	18	250 ± 50	378 ± 33	380 ± 31
		63	21 ± 2.5	383 ± 15	
	95/4/1	18	113 ± 7	270 ± 6	259 ± 16
		36	22 ± 1	248 ± 4	
	95/2.5/2.5	9	429 ± 20	265 ± 6	259 ± 15
		36	22 ± 1	248 ± 4	
		63	8.8 ± 0.3	264 ± 4	
	95/1/4	18	55 ± 3	207 ± 5	220 ± 18
		36	18 ± 0.5	233 ± 5	
Constant Copper Chromite	93/2.5/4.5	18	56 ± 4	208 ± 6	208 ± 6
		36	14 ± 0.5	208 ± 5	
	94/2.5/3.5	18	67 ± 2.5	226 ± 4	221 ± 7
		36	15 ± 0.5	216 ± 2	
	95/2.5/2.5	s e e	a b o v e		259 ± 15
	96/2.5/1.5	18	95 ± 5	253 ± 5	249 ± 11
		36	21 ± 2	244 ± 7	
	97/2.5/0.5	18	145 ± 6	298 ± 5	298 ± 12
		36	36 ± 4	298 ± 12	
Constant Carbon	93/4.5/2.5	18	93 ± 2	250 ± 3	241 ± 12
		36	18 ± 0.5	233 ± 2	
	94/3.5/2.5	18	91 ± 9	250 ± 8	260 ± 18
		36	28 ± 2	270 ± 8	
	95/2.5/2.5	s e e	a b o v e		259 ± 15
	96/1.5/2.5	18	100 ± 6	258 ± 5	257 ± 6
		36	24 ± 1	256 ± 3	
	97/0.5/2.5	18	106 ± 6	263 ± 3	263 ± 5

LIST OF ILLUSTRATIONS

CARBON ARC   COAXIAL SLOTTED DISKS

ARC REFLECTOR   IMAGE OF ARC &   SAMPLE
                       POSITION OF PELLET   REFLECTOR

RA-451,541-3
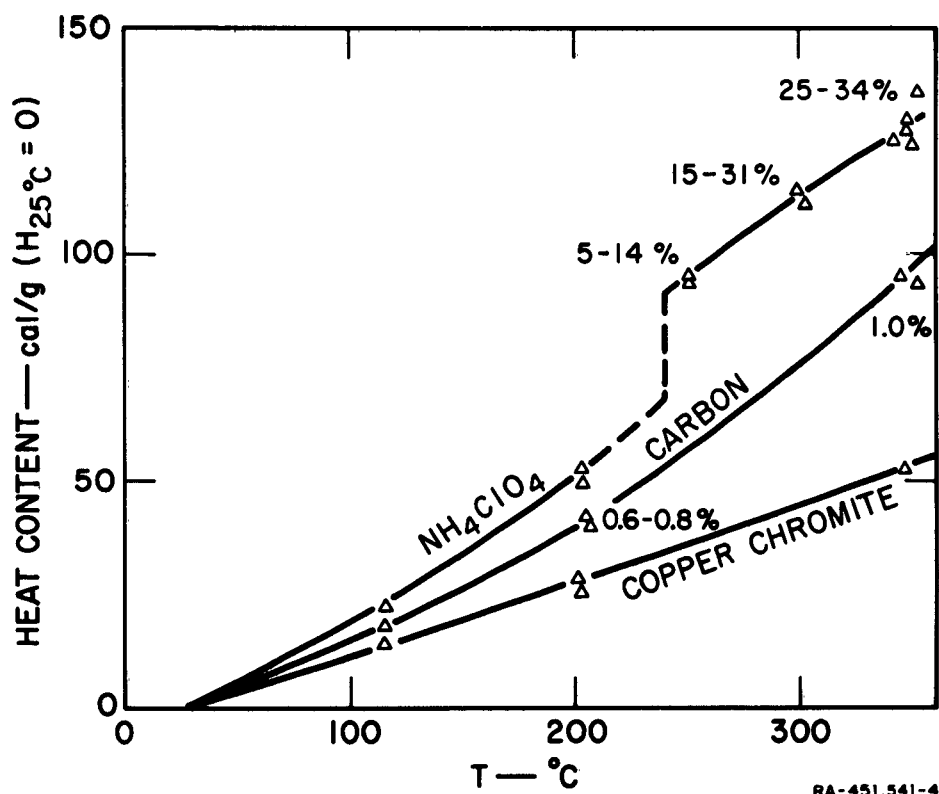
FIG. 1 SCHEMATIC DRAWING OF DOUBLE ELLIPSOIDAL CARBON ARC IMAGE SYSTEM

FIG. 2 HEAT CONTENTS OF AMMONIUM PERCHLORATE, COPPER CHROMITE, AND CARBON
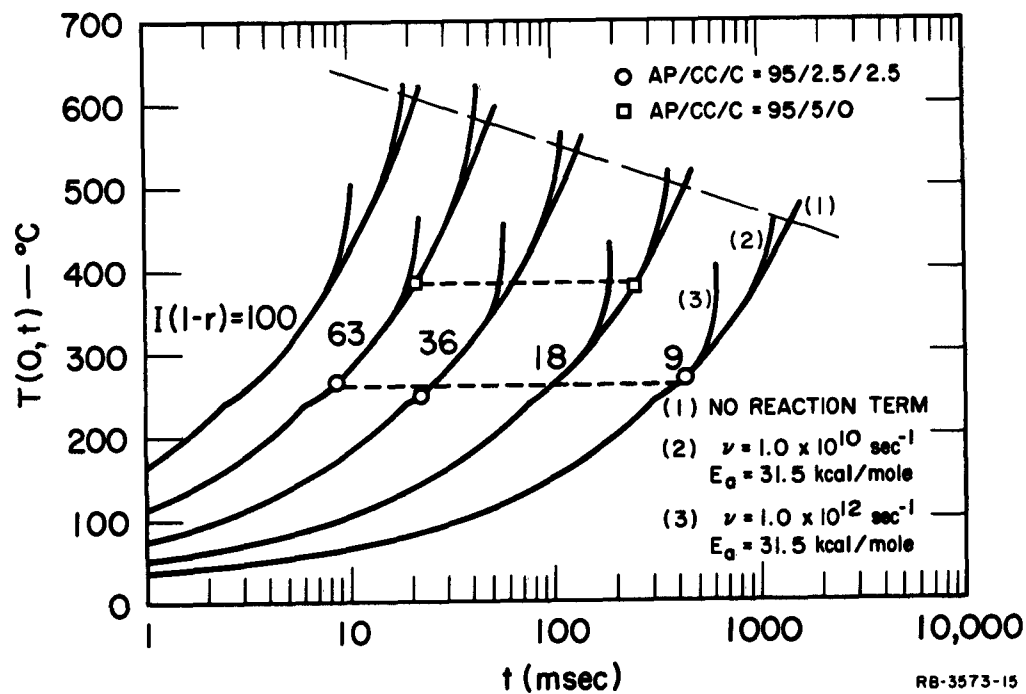(Percentages represent weight loss during heating)

700

600

500

$T(0,t) - °C$

400

300

200

100

0

○ AP/CC/C = 95/2.5/2.5
□ AP/CC/C = 95/5/0

(1)

(2)

(3)

I(1-r)=100   63   36   18   9

(1) NO REACTION TERM

(2) $\nu = 1.0 \times 10^{10}$ sec^{-1}
    $E_a = 31.5$ kcal/mole

(3) $\nu = 1.0 \times 10^{12}$ sec^{-1}
    $E_a = 31.5$ kcal/mole

1   10   100   1000   10,000

t (msec)

RB-3573-15

FIG. 3   SURFACE TEMPERATURE T(0,t) VERSUS TIME (units of I(1 - r) ARE cal/cm^2-sec)